- Hydrogen selenide; H₂Se; [7783-07-5]
- 2. Aqueous and non-aqueous solvents.

EVALUATOR:

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July 1987

CRITICAL EVALUATION:

Few measurements of the solubility of hydrogen selenide have been reported in the literature. At 298.15 K liquid hydrogen selenide has a lower vapor pressure than liquid hydrogen sulfide. Raoult's law leads one to expect that hydrogen selenide is likely to have a higher mole fraction solubility in a given solvent than hydrogen sulfide, at the same temperature and partial pressure of gas. This appears to be the case for eight of the nine non-aqueous solvents for which data is available. Hydrogen sulfide is, however, the more soluble in water under the conditions which have been investigated.

Devyatykh et al. (1) measured distribution constants for certain non-aqueous solvents. These can only be equated with Ostwald coefficients if it can be established that surface effects made negligible contribution to the chromatographic process and that conditions were close to equilibrium. In the absence of other data these measurements are best considered as an indication of approximate relative solubilities in different solvents. The following solvents were studied:

In all these solvents, with the exception of 1,2-benzenedicarboxylic acid, didecyl ester, hydrogen selenide has a higher distribution constant than hydrogen sulfide at 293.2 K.

Solubility in water at a partial pressure of 1.013 bar has been reported by McAmis & Felsing (2) for 287.7 to 308.2 K and by Dubeau *et al.* (3) for 298.2 to 343.2 K. There is, on the whole, good agreement between the two sets of measurements (see fig.7). Mole fraction solubilities for a partial pressure of 1.013 bar may be fitted to the following equation:

$$\ln x_{\text{H}_2\text{Se}} = 9.15 + 974/(\text{T/K}) - 3.542 \ln (\text{T/K}) + 0.00420 (\text{T/K})$$

$$\delta x_{\text{H}_2\text{Se}} = \pm 2.3 \times 10^{-5}$$

This equation is valid in the temperature range 287.7 to 343.2 K.

The value given by McAmis and Felsing for 308.2 K seems to be out of line with the data at higher temperatures by Dubeau and has not been used by the evaluator in the calculation of this smoothing equation.

McAmis & Felsing also investigated the solubility at 298.15 K and a total pressure of 1.013 bar in solutions of hydrogen iodide of concentrations to 2.73 mol dm^{-3} . Solubilities increase with concentration of hydrogen iodide and follow a Sechenov relationship very closely. They may be fitted to the equation:

 $\log_{10}(\text{concn. H}_2\text{S/mol dm}^{-3}) = -1.0788 + 0.04011 (\text{concn. HI/mol dm}^{-3})$

Standard deviation of log_{10} (concn. of $H_2S/mol\ dm^{-3}$) = ± 0.0035

These data for solutions of hydrogen iodide appear to be reliable and may be accepted on a tentative basis.

References

- Devyatykh, G.G.; Ezheleva, A.E.; Zorin, A.D.; Zueva, M.V. Zh. Neorgan. Khim. 1963, 8, 1307-1313.
 Russ. J. Inorg. Chem. 1963, 8, 678-682.
- 2. McAmis, A.J.; Felsing, W.A. J. Am. Chem. Soc. 1925, 4, 2633-2637.
- 3. Dubeau, C.; Sisi, J.-C.; Ozanne, N. J. Chem. Engng. Data 1971, 16, 78-79.

- Hydrogen selenide; H₂Se; [7783-07-5]
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CRITICAL EVALUATION:

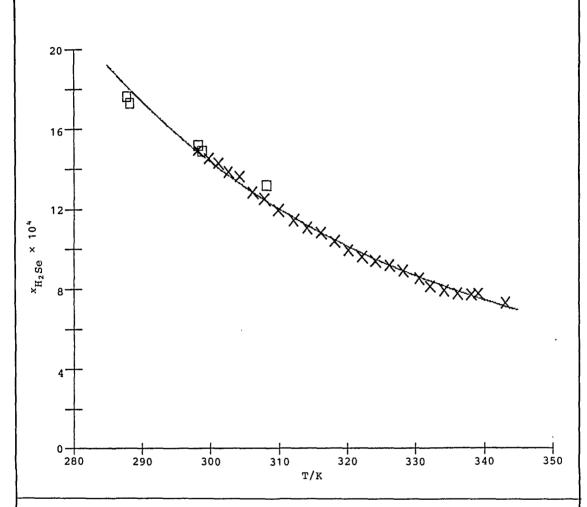


Fig. 7 <u>Variation with temperature of the mole fraction solubility of hydrogen selenide in water at a partial pressure of 1.013 bar</u>

Experimental points have been superimposed upon the curve corresponding to the equation:

$$\ln x_{\text{H}_2\text{Se}} = 9.15 + 974/(\text{T/K}) - 3.542 \ln (\text{T/K}) + 0.00420 (\text{T/K})$$

McAmis & Felsing (2)

X Dubeau et al. (3)

COMPONENTS:		ORIGINAL	MEASUREMENTS:	
 Hydrogen selenide; H₂Se; [7783-07-5] Various liquids 		Zorin,	ykh, G. G.; Ezho A. D.; Zueva, I J. Inorg. Chem. 8, 678-682.	•
VARIABLES:		PREPARED	BY:	
Temperature, pressure			P. G. T.	Fogg
EXPERIMENTAL VALUES:		·		
Solvent	^P H₂Se	/mmHg	Distribution constant vol _{H2} Se /vol _{solvent}	Heat of solution /kcal mol 1
2-Ethoxyethanol; C ₄ H ₁₀ O ₂ ; [110-80-5]	C	.3	14.42	- 1.6

Temperature = 293.2 K.

[98-95-3]

Nitrobenzene;

Liquid paraffin

1,1'-oxybis[2-chloroethane]; C4H8Cl2O; [111-44-4]

C6H5NO2;

760 mmHg = 1 atm = 1.013×10^5 Pa.

12.5

22.0

30.0

Distribution constants were measured between 278.2 K and 323.2 K with a total pressure of hydrogen selenide and carrier gas of about 760 mmHg. At a fixed temperature the distribution constants did not depart from the mean values by more than ±3%. These mean values were reported at one temperature only but heats of solution, said to have been calculated from the variation of distribution constants with temperature, were given. If it is assumed that distribution constants vary with temperature according to equations of the form:

0.2

0.2

0.3

$$\ln K = (-\Delta H/RT) + A$$

(cont.)

- 3.4

- 2.45

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A chromatographic method was used. Temperatures were controlled to ±0.5 K. The support phase consisted of Nichrome spirals. The carrier gas was either nitrogen or hydrogen. The volume, V_o , of the liquid phase was calculated from the weight of the column before and after filling with liquid and allowing to drain. The free volume, V_{q} , was equated with the retention volume for hydrogen The distribution constant, K, was calculated from the James and Martin equation:

$$V_{R} = V_{q} + KV_{\ell}$$

where $\mathbf{V}_{\mathbf{R}}$ is the retention volume for hydrogen selenide.

SOURCE AND PURITY OF MATERIALS:

- Prepared by hydrolysis of Al₂Se₃; purified by vacuum distillation; chromatographically pure.
- \mbox{H}_{2} and $\mbox{N}_{2}\colon$ passed through activated carbon and through molecular sieve.

ESTIMATED ERROR:

- 1. Hydrogen selenide; H₂Se; [7783-07-5]
- 2. Various liquids

ORIGINAL MEASUREMENTS:

Devyatykh, G. G.; Ezheleva, A. E.; Zorin, A. D.; Zueva, M. V.

Russ. J. Inorg. Chem. 1963, 8, 678-682.

EXPERIMENTAL VALUES:

where K is the distribution constant for a temperature T, ΔH is the heat of solution of hydrogen selenide in the solvent and A is a constant for the solvent, then distribution constants at any temperature in the range 278.2 K to 323.2 K may be estimated from a value at 293.2 K and the corresponding value of the heat of solution. The equation for K may be written in the form:

$$K = \exp [A + (B/T)].$$

The following values of A and B have been calculated by the compiler:

Solvent	A	в/к
2-Ethoxyethanol	- 0.079	806
1,1'-oxybis[2-chloroethane]	- 3.313	1712
Nitrobenzene	- 1.116	1234

In the opinion of the compiler these distribution constants can not be equated with Ostwald coefficients unless the assumption is made that equilibrium was established between gas and liquid phases under the conditions of the experiment.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Hydrogen selenide; H₂Se; [7783-07-5]2. Various liquids	Devyatykh, G. G.; Ezheleva, A. E.; Zorin, A. D.; Zueva, M. V. Russ. J. Inorg. Chem. 1963, 8, 678-682.
VARIABLES:	PREPARED BY:
Temperature	P. G. T. Fogg
EXPERIMENTAL VALUES:	
Solvent	Distribution constant Heat of solution vol _{H₃P} /kcal mol ⁻¹
	/vol _{solvent}
2-Furancarboxaldehyde; C ₅ H ₄ O ₂ ; [98-01-1]	22.5 -
1,2-Benzenedicarboxylic acid, didecyl ester; C ₂₈ H ₄₆ O ₄ ; [84-77-5]	28.5 -
Triethoxysilane; C ₆ H ₁₆ O ₃ Si; [998-30-1]	5.21 ~ 5.0
Silicic acid, tetraethyl ester; C ₈ H ₂₀ O ₄ Si; [78-10-4]	11.52 ~ 5.4

Temperature = 293.2 K.

Distribution constants were measured between 278.2 K and 323.2 K. The partial pressures of hydrogen selenide at which these measurements were made were not stated. The total pressure of hydrogen selenide and carrier gas was about 760 mmHg in each case. Distribution constants were reported at one temperature only but heats of solution, said to have been calculated from the variation of distribution constants with temperature, were given in two cases.

(cont.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A chromatographic method was used. Temperatures were controlled to $\pm 0.5~\rm K$. The support phase consisted of Nichrome spirals. The carrier gas was either nitrogen or hydrogen. The volume, $\rm V_{\ell}$, of the liquid phase was calculated from the weight of the column before and after filling with liquid and allowing to drain. The free volume, $\rm V_{g}$, was equated with the retention volume for hydrogen gas. The distribution constant, $\rm K$, was calculated from the James and Martin equation:

$$V_R = V_G + KV_{g}$$

where $\mathbf{V}_{\mathbf{R}}$ is the retention volume for hydrogen selenide.

SOURCE AND PURITY OF MATERIALS:

- Prepared by hydrolysis of Al₂Se₃; purified by vacuum distillation; chromatographically pure.
- ${
 m H_2}$ and ${
 m N_2}$: passed through activated carbon and through molecular sieve.

ESTIMATED ERROR:

- 1. Hydrogen selenide; H₂Se; [7783-07-5]
- 2. Various liquids

ORIGINAL MEASUREMENTS:

Devyatykh, G. G.; Ezheleva, A. E.; Zorin, A. D.; Zueva, M. V.

Russ. J. Inorg. Chem. 1963, 8, 678-682.

EXPERIMENTAL VALUES:

If it is assumed that distribution constants vary with temperature according to equations of the form:

$$\ln K = (-\Delta H/RT) + A$$

where K is the distribution constant for a temperature T, ΔH is the heat of solution in the solvent and A is a constant for the solvent, then distribution constants at any temperature in the range 278.2 K to 323.2 K may be estimated from a value at 293.2 K and the corresponding value of the heat of solution. The equation for K may be written in the form:

$$K = \exp [A + (B/T)].$$

The following values of A and B have been calculated by the compiler:

Solvent	А	В/К
Triethoxysilane	- 6.936	2518
Silicic acid, tetraethyl ester	- 6.830	2719

In the opinion of the compiler these distribution constants can not be equated with Ostwald coefficients unless the assumption is made that equilibrium was established between gas and liquid phases under the conditions of the experiment.

336 Hydrogen Selenide COMPONENTS: ORIGINAL MEASUREMENTS: Hydrogen selenide; H2Se; McAmis, A.J.; Felsing, W.A. [7783-07-5] J. Am. Chem. Soc. 1925, 4, 2633-2637 Water; H₂O; [7732-18-5] 2. VARIABLES: PREPARED BY: C.L. Young Temperature EXPERIMENTAL VALUES: 760 mmHg = 101.3 kPa^PH₂Se T/°C Moles H₂Se per dm³ of soln. + T/K No. of Mole fraction of H₂Se, $x_{\rm H_2Se}$ determinations (Av. devn.%)

14.6 287.8 5 (0.14) 0.09789 0.00176 288.2 0.09611 15.0 5 (0.29) 0.00173 25.0 298.2 6 (0.21) 0.08415 0.00152 25.6 298.8 4 (0.41) 0.08277 0.00149 35.0 308.2 4(0.23)0.07317 0.00132

it appears that this concentration is, as indicated, in units of mol dm^{-3} (soln) rather than mol dm^{-3} (water). It has been assumed that the molar volume of the solution is the same as that of water for the purpose of calculating the mole fraction.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Hydrogen selenide bubbled into water until saturated at the stated temperatures. Samples of saturated solutions removed and analysed either volumetrically or gravimetrically. The gravimetric method was based on the reaction between silver nitrate and hydrogen selenide. In the volumetric method saturated sample added to an excess of standard iodine solution, the selenium allowed to settle, and the excess iodine solution titrated against thiosulfate ESTIMATED ERROR: solution.

SOURCE AND PURITY OF MATERIALS:

- Prepared by action of water on aluminium selenide.
- 2. Boiled and distilled.

 $\delta T/K = \pm 0.1$; $\delta x_{H_2Se} = \pm 2$ %

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Hydrogen Selenide		
COMPONENTS: 1. Hydrogen selenide; H ₂ Se [7783-07-5] 2. Water; H ₂ O; [7732-18-5]	;	RIGINAL MEASUREMENTS: Dubeau, C.; Sisi, JC.; Ozanne, N. J. Chem. Engng. Data 1971, 16, 78-79.
VARIABLES: Temperature	P	REPARED BY: C. L. Young
EXPERIMENTAL VALUES: Partial T/°C T/K	_	1 atm = 101.3 kPa Mole fraction of hydrogen selenide, $x_{\rm H_2Se}$
25.1 298.25 26.6 299.75 28.0 301.15 29.5 302.65 31.1 304.25 33.0 306.15 34.7 307.85 36.7 309.85 39.0 312.15 41.0 314.15	0.08347 0.08289 0.08062 0.08031 0.07943 0.07909 0.07709 0.07675 0.0757 0.07533 0.07091 0.07133 0.06913 0.06613 0.06647 0.06613 0.06331 0.06097 0.06141	0.00150 0.00149 0.00145 0.00145 0.00143 0.00139 0.00138 0.00136 0.00128 0.00125 0.00125 0.00125 0.00125 0.00120 0.0014 0.00114 0.00114 0.00110 0.00111
METHOD/APPARATUS/PROCEDURE: Sample of water saturated hydrogen selenide at lowes experimental temperature a sample withdrawn after 15 Temperature increased and 4 hrs another sample withd Samples analyzed by gravim analysis using silver nitr precipitating agent. Det in source.	with t nd days. after rawn. etric ate as ails	OURCE AND PURITY OF MATERIALS: 1. Matheson sample, purity 98 mole per cent. 2. Deoxygenated and demineralised. STIMATED ERROR: &T/K = ±0.1; &S = ±1% up to 50 °C and ±2% above 50 °C (estimated by compiler). REFERENCES:

- 1. Hydrogen selenide; H₂Se;
 [7783-07-5]
- 2. Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Dubeau, C.; Sisi, J.-C.; Ozanne, N.

J. Chem. Engng. Data

1971, 16, 78-79.

EXPERIMENTAL VALUES:

T/°C	T/K	Solubility [#]	Mole fraction § of hydrogen selenide, x $^{H_{2}}$ Se
43.0	316.15	0.05922	0.00107
		0.06033	0.00109
45.0	318.15	0.05833	0.00105
		0.05643	0,00102
47.0	320.15	0.05544	0.00100
1		0.05504	0.000992
49.0	322.15	0.05361	0.000967
		0.05297	0.000955
51.0	324.15	0.05249	0.000947
		0.05161	0.000931
53.0	326.15	0.05079	0.000916
		0.05073	0.000915
55.0	328.15	0.05012	0.000904
		0.0487	0.000878
57.4	330.55	0.04672	0.000843
		0.04744	0.000856
59.0	332.15	0.04587	0.000827
		0.04384	0.000791
61.0	334.15	0.04465	0.000805
		0.04299	0.000775
63.0	336.15	0.04397	0.000793
65.0	220 15	0.04197	0.000757
65.0	338.15	0.04377	0.000790
		0.04214	0.000760
66.0	339.15	0.04255 0.04228	0.000767
00.0	232.12	0.04228	0.000763 0.000770
		0.04269	0.000770
70.0	343.15	0.04017	0.000794
/0.0	242.13	0.0401/	0.000725

[#] Moles of H₂Se per dm³ of solution.

 $^{^\}S$ Calculated by compiler assuming that 1 dm³ of solution contains 55.4 moles. It seems likely that the volume was measured at room temperature. The effect of the H₂Se on the density of water has been neglected.

Hydrogen Selenide 339 ORIGINAL MEASUREMENTS: COMPONENTS: McAmis, A.J. Felsing, W.A. Hydrogen selenide; H2Se; (7783-07-51)J. Am. Chem. Soc. 1925, 4, 2633-2637 Hydrogen iodide; HI; [10034-85-2] Water; H₂O; [7732-18-5] VARIABLES: PREPARED BY: Concentration of comp. 2. C.L. Young EXPERIMENTAL VALUES: T/°C Conc. of H₂Se, S /mol dm⁻³ (soln) T/K Conc. of No. of HI/mol dm-3 determinations (Av.devn. %) 0.20 298.2 25 4 (0.31) 0.08478 0.08634 0.40 4 (0.31) 2.73 4 (0.82) 0.11012 Total pressure = 760 mmHg = 1.013 bar AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: Hydrogen selenide bubbled into Prepared by action of water on hydriodic acid until saturated at aluminium selenide. the stated temperature. Samples of saturated solutions removed and 2.and 3. analysed by volumetric method. A Hydrogen iodide prepared by reaction of red phosphorus saturated sample was added to an excess of standard iodine solution, and iodine in the presence the selenium allowed to settle and of water was dissolved in the excess iodine solution titrated conductivity water. against thiosulfate solution. ESTIMATED ERROR:

 $\delta T/K = \pm 0.1; \ \delta S = \pm 2\%$